Pyrolysis of Broiler Manure: Char and Product Gas Characterization

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Value-added materials produced from broiler manure can be a renewable alternative to its problematic disposal. Pyrolysis of broiler manure (litter and cake) produces char, bio-oil, and biogas. In this study broiler manure chars were characterized for their ability to adsorb selected metal ions. Char yields for pelletized broiler manure slowly pyrolyzed at 700 and 800 °C for 1 h ranged between 29.6% and 33.5%. Surface areas for the broiler litter and cake decreased with pyrolysis temperature with 238 and 318 m^2/g and 199 and 261 m^2/g for 700 and 800 °C, respectively. Broiler manure chars removed significantly more metal ions from solution (up to 0.91 mmol/g Cu^{2+} and 0.96 mmol/g Zn^{2+}) when compared to chars produced from coal, wood, or coconut shells (up to 0.0 mmol/g Cu^{2+} and 0.10 mmol/g Zn^{2+}). Composition of the biogas generated during fast pyrolysis between 700−900 °C, as a measurement of its energy potential, was also determined. The major components of the noncondensable gas produced during fast pyrolysis of broiler manure, included CO, CO_2, low molecular weight hydrocarbon gases, and H_2. Except for CO, noncondensable gases increased with pyrolysis temperature.

Introduction

Pyrolytic products or chars are low porosity, low surface area materials that are intermediate products in the development of activated carbons. They are not commonly used in industry for purification and chemical recovery operations or environmental remediation, as are the more structurally developed activated carbons. Toxic metals contamination of various water sources is a significant problem in many parts of the United States. Chars, which can be produced from a number of precursor materials including coal, biomass, and municipal wastes, have not been examined for remediation of this problem. There are few if any commercial outlets for chars because of their inferior adsorption characteristics compared to activated carbon. While carbon production is an expanding industry in the United States, with a present production rate of over 400 million pounds a year and a growth rate of over 3% annually, char production is simply an intermediate step in carbon manufacture and has no significant presence in the marketplace. Besides a char product, pyrolysis also delivers biosyn-gas and bio-oil which can have an associated energy potential.

The production of pyrolytic products, in the form of chars, is an age-old art. Char, when produced in the absence of air by nonoxidative carbonization or pyrolysis, is a relatively inactive material possessing a surface area limited to several square meters per gram. Chars are normally produced to reduce the volume and mass of a particular feedstock and provide a soil amender that improves the physical and nutritive properties through its ash content of hard, compact soils with a high clay content or highly porous soils with a high silica or sand content. Because chars have poorly developed internal structure, they adsorb few if any metal ions or organic compounds and nonpolar materials from either liquid or gaseous media.

Very few studies have evaluated animal waste as source of pyrolytic products or their respective activated carbons. Animal waste generally has lower elemental carbon content and may produce lower char yields than plant material when both sources are pyrolyzed under the same time and temperature conditions. Cattle manure has been used[1] to produce a pyrolysis product as a soil amender due to its high content in phosphate ion, organic nitrate, and potassium ion. The pyrolysis product, produced by heating cattle manure to 380 °C in an atmosphere of limited air, had a very low surface area of 2.2 m^2/g, an ash content of 25.6%, and an elemental carbon content of 49.2%. The production of pyrolyzed cattle manure was also described over the temperature range of 250−800 °C in closed containers.[2] Surface areas were also low (<20 m^2/g) over this temperature range. The pyrolyzed cattle manure had high ash content (up to 60%), a high pH (>10), and a total carbon content of less than 40%. With a subsequent chemical activation step using zinc chloride, BET values surpassed 2000 m^2/g for chemically activated chars from cattle-manure.[3] Alternative to chemical activation, steam activation yielded low surface area (60.5 m^2/g) for a carbon product produced from steam-activated poultry droppings in a fluidized bed reactor.[4] It was concluded that poultry droppings will yield only a very low grade carbon mainly because of its low surface area and high ash content. More recently, Koutcheiko et al.[5] pyrolyzed chicken manure to produce a char with BET surface area of 4 m^2/g which augmented by subsequent separate consecutive activations, using NaOH and CO_2. The resulting product was a demineralized activated carbon with BET of 877 m^2/g and a mineral content of 10% wt. Sewage sludge was used by Jindarom et al.[6] to produce a char under either N_2 or CO_2 atmospheres as a potential adsorbent for dye removal. Maximum surface area of mainly mesopores was 60.7 m^2/g, and dye adsorption was found to increase with pyrolysis temperature.

While various methodologies exist for the creation of activated carbons from plant or plant-derived material that are effective in the adsorption of metal ions, there remains a need to create lower cost pyrolytic products, such as chars, from alternate sources of carbonaceous material that are in great abundance and that have enhanced adsorption properties toward metal ions. Additionally, thermo-chemical conversion of biomass is becoming increasingly popular as an alternative means

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for renewable energy production and some studies in the literature report the thermochemical conversion of animal manures and sewage sludges in particular.[7−10] The thermochemical conversion of biomass for bio-oil and/or biogas production generates a char material that should be characterized for its potential use as adsorbent. With these conversion technologies for energy production from bio-oil and/or biogas, chars are also generated for which their use as an adsorbent needs to be investigated. Whether chars are produced as the primary choice material from pyrolysis or considered a byproduct, thermochemical conversion as a whole benefits from the exploration of all generated streams and their respective potential use. The objective of this study was to produce value-added chars from poultry manure with excellent metal ion adsorptive properties. Additionally, the biogas resulting from the pyrolysis process was further characterized for its potential as a fuel source.

Materials and Methods

Raw Material and Sample Preparation. Broiler cake and litter samples were obtained from the USDA-ARS, Poultry Research Unit, Starkville, MS. Broiler cake results from partial cleaning of the top layer in a poultry house and litter results from a complete cleaning of the facility. Cake consists of bird droppings, feathers, and small amounts (<5%) of bedding material while litter contains larger amounts of bedding material (20−30%), usually made of wood shavings, typically soft wood, such as pine. Samples were milled in a Retsch cross-beater mill (Glen Mills, Clifton, NJ) to a particle size of less than US 20 mesh (<1 mm). Ground samples were then pelletized in a PMCL5 Laboratory pellet mill (California Pellet Mill, Merrimack, NH) equipped with a 3/16 in. die plate. Sample moisture content was monitored with a Sartorius moisture analyzer model MA 51 (Sartorius, Brentwood, NJ). The pellets produced were cylinders of 3/16 in. diameter and 3/16 in. length. Pelletized poultry cake and litter samples were placed in a ceramic evaporating dish and placed in a Lindberg bench furnace equipped with a retort (Lindberg/Blue M, Waterton, WI). Pellets were pyrolyzed (under slow pyrolysis conditions) at either 700 or 800 °C for one hour under a flow of nitrogen gas set at a flow rate of 0.1 m^3/h. Chars were allowed to cool to room temperature overnight in the retort. Samples were washed with 0.1 M HCl and subsequently given three separate water washings before being dried overnight at 80 °C.

Physical and Chemical Properties. The charcoals resulting from slow pyrolysis were evaluated for select physical and chemical properties that include char yield, surface area, apparent (bulk) density, attrition (hardness), and pH. Surface area measurements were obtained from nitrogen adsorption isotherms at 77 K using a Nova 2000 surface area analyzer (Quantachrome Corp., Boynton Beach, FL). Specific surface areas (S_{BET}) were taken from adsorption isotherms using the Brunauer, Emmett, and Teller (BET) equation. Bulk density and attrition were determined as in the methods described in Lima and Marshall.[11] A Thermo Orion pH meter was used to measure pH, where 0.5 g of sample was placed in 50 mL of deionized water, covered with parafilm, and allowed to equilibrate by stirring at 300 rpm for 72 h.

Adsorption Isotherms. Adsorption isotherms were run for copper ion per the method described in Lima and Marshall.[11] Adsorption capacities (Q_0) and affinity constants (b) were calculated by fitting the isotherm data to the nonlinear Langmuir adsorption model:

$$q_e = Q_0 b C_e/(1 + bC_e) \quad (1)$$

where q_e = amount of solute adsorbed per unit weight of adsorbent in mmol/g; C_e = equilibrium concentration of solute in mM; Q_0 = monolayer adsorption capacity of adsorbent for solute in mmol/g, and b = constant related to the free energy of adsorption in L/mM. The nonlinear least-squares regression method of Marquardt was implemented using Sigma Plot v. 7.101 for Windows 2000 (SPSS Inc. Chicago, IL). A correlation coefficient (r^2) and a probability value (p-value) representing the goodness of fit of the Langmuir model to the data were obtained.

Metals Adsorption. Chars were analyzed for metal ion uptake using 20 mM individual metal solutions of cadmium chloride ($CdCl_2$), copper chloride ($CuCl_2$), nickel nitrate [$Ni(NO_3)_2$], or zinc chloride ($ZnCl_2$), which were made up in an 0.07 M sodium acetate−0.03 M acetic acid buffer (pH 4.8). Multiple metal solutions included all four metal ions at 5 mM each. Adsorption assays and metal concentration were determined as in the method by Lima and Marshall.[11]

Determination of Biogas Composition. Biogas produced from the same two broiler manure samples was determined by fast pyrolysis. A CDS analytical (Oxford, PA) pyroprobe was used for the fast pyrolysis. It consisted of a 1-cm quartz tube heated by a platinum filament of 2−3 mm diameter, which is capable of maintaining up to 1200 °C temperature at a nominal heating rate of 20 °C/ms. Pulverized samples were sifted and particle sizes with 90% passing a 500 μm screen were used. The average weight charged into the pyrolyzer (PY) was about 1 mg (0.96−1.12) and occupied about 1−1.5 mm in height in the quartz tube holder over packed quartz wool. Helium, the carrier gas for the GC, was also used to purge air in the sample prior to pyrolysis and the pyrolysis gas yield to the GC. Although the nominal heating rate is about 20 °C ms^{-1}, the sample heating rate can be much lower and typically estimated[12] at 300 °C s^{-1}. The experimental sample preparation procedure is reported in Boateng et al.[13] and is consistent with other reports.[12] Using samples weighing less than 2 mg does not significantly change gas yield.[12] The pyrolyzer was interfaced to a gas chromatograph (SRI, CA). The pyroprobe/gas chromatograph (PY-GC) system allowed for a variety of compounds formed during flash pyrolysis to be characterized. The noncondensable gas products from pyrolysis were separated using a Shincarbon ST 80/100, 2 m × 2.0 mm packed column (Restek, Bellefonte, PA). The GC was programmed to maintain 45 °C for 3 min after injection, followed by a 10 C/min ramp to 250 °C, followed by holding at 250 °C for 10 min, yielding a total time of 34.4 min. Hydrogen was detected using the TCD SRI Instruments Wheatstone bridge with four filaments. The yields of the major noncondensable gas products from primary and secondary pyrolysis reactions were quantified by calibration with a standard gas mixture consisting of CO, CO_2, H_2, CH_4, C_2H_4, C_2H_6, C_3H_8, and C_4H_{10} in helium (custom-mixed by Scott Specialty Gases, Plumsteadville, PA). Gas yields were quantified on the basis of a linear relationship between the mass and area counts of the programs. The coefficient of determination, R^2, for the linear fits ranged between 70% (CO) to 97% (CH_4). Char yield was determined gravimetrically. Tests were run in triplicate, and average values are reported, for three pyrolysis temperatures: 700, 800, and 900 °C, for 20 s retention time. At this time there was no further change and therefore the devolatilization reaction was complete.

Results and Discussion

1. Physical Properties of Char. Pyrolysis is a series of cleavage reactions and polymerization reactions that make a

Table 1. Select Physical and Chemical Properties at Two Different Pyrolysis Temperatures, PT, 700 and 800 °C[a]

PT	sample	Y (%)	wt loss (%)	BET (m^2/g)	PM %	BD (g/cm^3)	A (%)	pH
700 °C	broiler cake	40.3	24.5	318 ± 15	88.4 ± 0.4	0.54 ± 0.00	15.1 ± 0.2	8.6
	broiler litter	40.7	17.7	238 ± 13	90.4 ± 6.6	0.60 ± 0.00	14.4 ± 2.0	8.1
	coal	78.3	22.3	3.8 ± 2		0.42 ± 0.00	34.1 ± 3.0	4.2
	coconut shell	27.6	0.0	35 ± 12	34.6 ± 2.8	0.61 ± 0.00	20.5 ± 2.9	6.6
	wood	25.3	4.8	301 ± 24	86.3 ± 10.0	0.38 ± 0.01	23.4 ± 0.3	5.1
800 °C	broiler cake	39.3	24.5	261 ± 47	93.3 ± 4.9	0.53 ± 0.00	7.6 ± 2.6	9.4
	broiler litter	39.4	17.5	199 ± 33	84.9 ± 3.2	0.62 ± 0.01	7.7 ± 0.3	9.1

[a] Physical and chemical properties of poultry manure-based chars and chars made from traditional sources (coal, coconut shell, wood): yield, Y; percent loss from acid washing, wt loss; BET surface area; percent micropores, PM; bulk density, BD; and attrition, A; pH.

fixed carbon structure involving both carbonization and devolatilization processes. Carbonization is the stripping off of noncarbon atoms, like H, O, N, and S, and halides to create a purer carbon form. During devolatilization, the physical vaporizing of free carbon structures or weakly bonded carbon chains (volatile matter) occurs. Broiler litter and cake chars were analyzed for their physical and chemical properties, and data are summarized in Table 1. Char yield decreased slightly with pyrolysis temperature and was slightly lower for broiler cake char than for broiler litter chars. For 700 °C pyrolysis temperature, char yields for the broiler manure chars were much larger than those found for the plant-based chars. Nonetheless, weight losses from acid washing were larger for the broiler manure chars than their plant counterparts (wood and coconut shells) (Table 1). Broiler manure contains much higher amounts of inorganic compounds than either wood or coconut shells, which are removed during the acid wash step. Coal char yields were highest with significant amounts of inorganic material also removed by the acid wash as demonstrated by the percentage losses (Table 1). In previous studies Lima and Marshall[14,15] reported large ash values present in poultry manure carbons as a characteristic of the starting material. For this reason, both chars and carbons made from these types of precursors should be acid washed to partially remove excess levels of inorganic material that can potentially interfere with its use as an adsorbent material. Additionally, the presence of this inorganic fraction is responsible for the high pH values observed for broiler manure char pH. Values of pH were higher for broiler cake than broiler litter due to larger amounts of inorganic material in the former. Surface area (BET) values for both broiler litter and cake chars as well as for the wood char were unexpectedly high since chars are typically low porosity materials. BET surface areas for the chars produced in this study were greater than 199 m^2/g, even as high as 318 m^2/g, and a largely microporous structure was observed where 85 to 90% of pores were in the micropore size range (Table 1). With the exception of wood chars which also displayed much higher than expected BET values, the plant based chars contrasted with the broiler manure chars in that BET surfaces areas observed were significantly lower, ranging from 3.8 m^2/g to 35 m^2/g. Surface area was significantly higher for broiler cake char than for broiler litter and it decreased with pyrolysis temperature (Table 1). BET values for broiler cake chars at 318 m^2/g compare very favorably with the highest BET values reported for broiler litter-based activated carbon[14] of 548 m^2/g (activated for 60 min under a water flow of 3 mL/min). Attrition was lower for the broiler manure chars than the reference chars and contrary to what would be expected, attrition decreased with pyrolysis temperature. It is believed that attrition values are directly influenced by both the starting material and the pelletization process. Commonly, attrition is lower for harder materials and denser pellets. Coconut shells, wood, and coal are both harder materials than broiler manure. Therefore the lower attrition values of the latter are likely due to other properties related to the composition of the starting material, which produces a more cohesive pellet and yield a char more resistant to friction than the harder plant material char. It is important to add that attrition of wood- and coconut shell-chars in their native form (ground to 18 × 40 mesh or 0.47 to 1.119 mm) without pelletization instead of ground to a powder and subsequently pelletized) should be significantly reduced. Overall, comparing properties of the broiler manure char with those found by Lima and Marshall[16] for activated carbons of the same material, it is observed that in the char, yield and bulk density are higher and surface area and attrition are lower. During pyrolysis or charring, carbon structure rearranges and condenses to a higher density, producing a more stable amorphous graphitic carbon structure. Further activation allows for pore development rendering the carbons less dense, more porous, and less resistant to abrasion. Previous work[17] has estimated production costs for broiler manure carbons at $0.65/lb. This value compared favorably well with other published studies in the literature on the cost of manufacturing carbons from pecan shells, almond shells, and sugar cane bagasse.[17] A lower cost of production for the broiler manure char is estimated since the activation step is eliminated and higher yields are obtained.

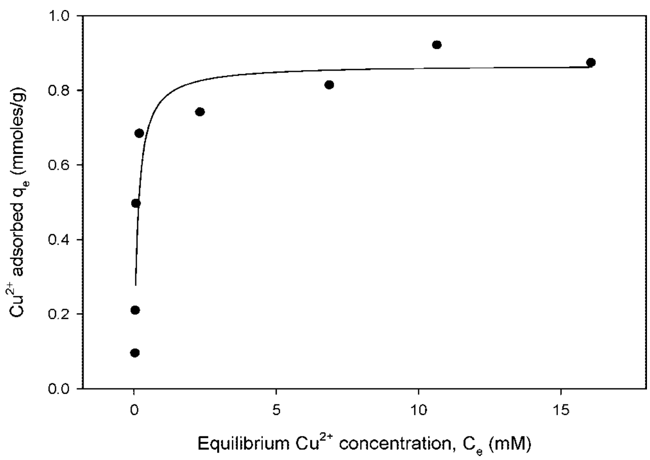

Figure 1. Copper ion isotherm for broiler cake char fitted to the Langmuir model.

Table 2. Langmuir Parameters for Copper Ion Adsorption: Adsorption Capacity Q_0 and Goodness of Fit Parameters r^2 and p, for Broiler Litter and Cake Chars Pyrolyzed at 700°C

sample	Q_0	b	R^2	p
broiler cake char	0.87	8.25	0.87	0.0008
broiler litter char	0.78	6.60	0.86	0.0009

2. Adsorption Properties of Char. Adsorption capacity (Table 2) for copper ion (Q_0) was calculated from the adsorption isotherm, by fitting data to the nonlinear Langmuir adsorption model (Figures 1 and 2). It can be seen from the regression parameters (r^2 and p-values) that the nonlinear regression model

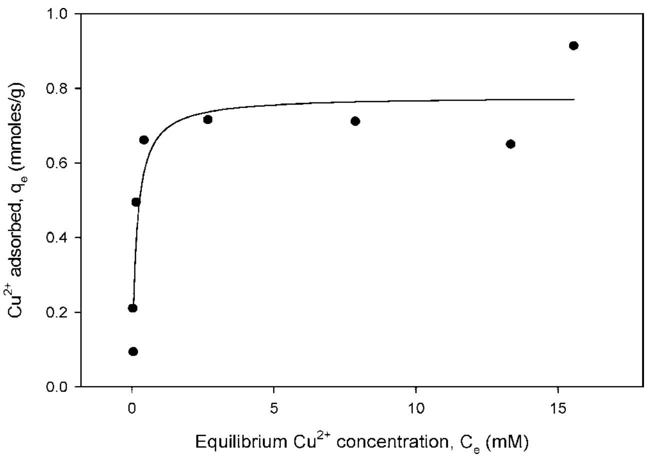

Figure 2. Copper ion isotherm for broiler litter char fitted to the Langmuir model.

Table 3. Metal Ion Adsorption of Chars Made from Poultry Manure and Chars Made from Traditional Sources (Coal, Coconut Shell, Wood) in mmol/g Char, at Two Different Pyrolysis Temperatures, PT, 700 and 800 °C

PT	sample	Cu^{2+}	Cd^{2+}	Ni^{2+}	Zn^{2+}
700 °C	broiler cake	0.91	0.64	0.10	0.96
	broiler litter	0.58	0.45	0.25	0.72
	coal	0.00	0.05	0.13	0.03
	coconut shell	0.00	0.04	0.13	0.10
	wood	0.00	0.03	0.20	0.05
800 °C	broiler cake	1.05	0.80	0.13	0.80
	broiler litter	0.68	0.43	0.03	0.43

fits the copper ion adsorption data well for both broiler litter and cake chars. Adsorption capacity toward copper ions was higher for the cake char than the litter char. This difference is linked to the presence of larger amounts of wood in litter than cake samples and, as will be discussed later, the reduced ability for metal ion uptake by wood-based chars. Copper ion saturation levels for the broiler manure chars can be extracted from the adsorption capacity values. For the broiler litter and cake chars, saturation occurred at a concentration of or around 0.8−0.9 mmoles Cu^{2+} per gram of char (Figures 1 and 2). Albeit high concentrations of this or other metals are not commonly found in waste waters, capacity values give an indication of how much could be adsorbed in a worst case scenario. The chars were further tested for their ability to adsorb three other metal ions at 20 mM, and adsorption efficiencies toward Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} are reported in Table 3. Broiler litter and cake chars generally showed good metal ion adsorption at pH 4.8 with the exception of nickel. Broiler cake adsorbed more metal ion than litter and both adsorbed significantly more metal ion than any of the reference chars (Table 3). With the exception of zinc ions, adsorption, in general, improved when pyrolysis temperature was increased from 700 to 800 °C. During pyrolysis, planar sheets of graphite plates form and either stack upon each other or form "v-shapes". Interbonding occurs by aliphatic dislocations (imperfection) of plates held together by weak atomic forces called London dispersion forces. Inorganic constituents, such as phosphorus, contained in the manure are either physically "trapped" or covalently (chemically) bound within the lattice structure. The presence of covalently bound phosphorus, primarily in the form of phosphate ion, can create centers of negative charge on the carbon. These centers of negative charge can readily adsorb or ionically bind positively charged ions such as copper. Table 4 reports the composition of both chars in certain elements, with larger amounts of each one found in the

Table 4. Broiler Litter and Cake Char Elemental Composition in Phosphorous (P), Calcium (Ca), Magnesium (Mg), Sulfur (S), and Potassium (K) in mg/g Char

	P	Ca	Mg	S	K
litter	36.8 ± 2.7	53.0 ± 4.0	14.2 ± 1.2	17.3 ± 2.3	42.0 ± 5.3
cake	49.2 ± 10.6	68.5 ± 15.5	22.2 ± 6.1	20.0 ± 1.7	36.5 ± 5.5

Table 5. Percent Metal Ion Adsorption Efficiencies of Broiler Manure Chars and Chars Made from Traditional Sources (Coal, Coconut Shell, Wood) at Two Different Pyrolysis Temperatures, PT, 700 and 800 °C, for Solutions Containing Only a Single Metal Ion at 5 mM Concentration

PT	sample	Cu^{2+}	Cd^{2+}	Ni^{2+}	Zn^{2+}
700 °C	broiler cake	95.4	83.2	6.6	89.8
	broiler litter	95.0	82.3	5.1	90.9
	coal	0.0	12.8	0.5	2.6
	coconut shell	3.1	13.5	0.0	0.5
	wood	6.3	13.3	0.0	1.8
800 °C	broiler cake	97.9	89.4	11.2	92.5
	broiler litter	86.9	59.9	6.0	75.7

Table 6. Percent Metal Ion Adsorption Efficiencies of Broiler Manure Chars and Chars Made from Traditional Sources (Coal, Coconut Shell, Wood) at Two Different Pyrolysis Temperatures, PT, 700 and 800 °C, for Solutions Containing Four Metal Ions at 5 mM Each

PT	sample	Cu^{2+}	Cd^{2+}	Ni^{2+}	Zn^{2+}
700 °C	broiler cake	71.1	18.8	3.8	23.7
	broiler litter	66.1	18.1	3.6	25.2
	coal	0.6	0.3	0.7	1.0
	coconut shell	0.2	0.9	0.7	3.8
	wood	4.0	0.0	0.0	2.4
800 °C	broiler cake	69.1	8.1	7.0	18.1
	broiler litter	39.6	4.9	10.8	11.0

broiler cake char (potassium excluded). From Table 4 it can be seen that the phosphorus content of broiler litter and cake chars ranges between 3.7% and 5% by weight. In contrast, chars produced from traditional sources, such as coal, coconut shell, and wood, generally have less than 0.2% phosphorus. Chars were also analyzed for metal ion uptake using less than saturating concentrations of metal ions with 5 mM solutions rather than 20 mM solutions. Tables 5 and 6 report adsorption values individually and in competition, respectively, as percent metal ion adsorbed. In competition mode, the chars were placed in solutions containing each of the four metal ions at concentrations of 5 mM per metal ion with a total metal ion concentration of 20 mM. A comparison across all metal ions demonstrates strong adsorption of copper and zinc by the broiler litter and cake chars and less adsorption for cadmium and zinc ions. Generally, affinity toward metal ions was highest for copper, followed by zinc, and then cadmium ions. Chars performed better when exposed to individual solutions of each metal ion than when exposed to all at the same time. In competition mode copper ions appeared to still be the choice for removal and the presence of other metal ions had little effect on its binding. This same trend was also observed in previous studies by Lima and Marshall.[16] There is no apparent reason why nickel ions bind much less readily than the remaining three metal ions in this study, as it is an ion of similar size and weight. Similar results were observed by Brown and Lester[18] with activated sludge, Ho et al.[19] with sphagnum moss, and Lima and Marshall[16] with poultry manure carbons. Reference chars adsorbed negligent amounts to none when exposed to the four metals at once.

3. Yields for Noncondensable Gas, Char, and Tar. In addition to char characterization, two other products of pyrolysis, bio-oil and noncondensable gas were also quantified for yield,

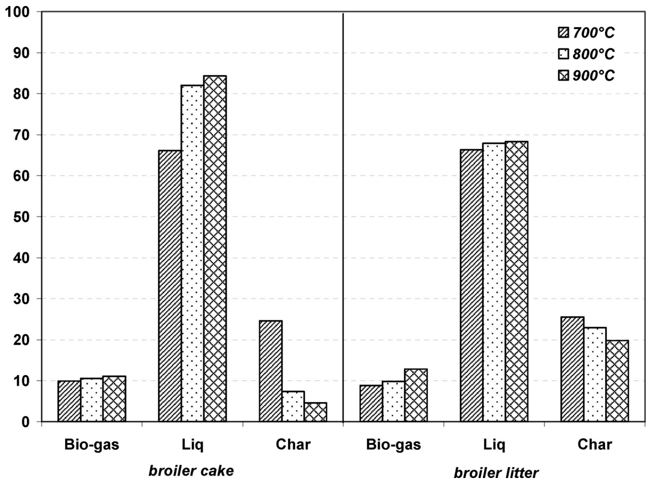

Figure 3. Yields for noncondensable gas, char, and bio-oil as a function of pyrolysis temperature for broiler cake and litter samples.

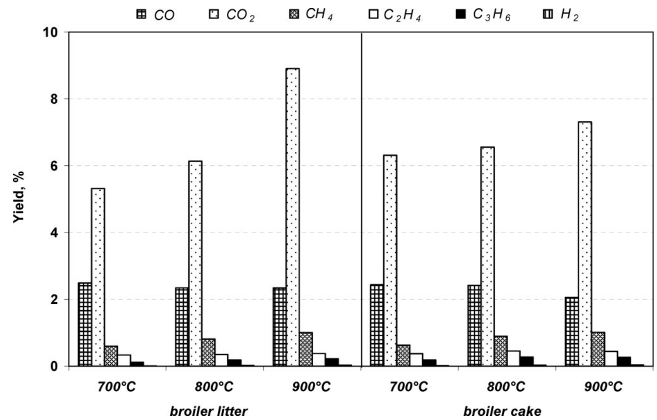

Figure 4. Percent composition of quantified noncondensable gas yields as a function of pyrolysis temperature and for broiler cake and litter samples.

and composition of the noncondensable gas was characterized. During pyrolysis, carbon atoms fixed within the calcined structure via gas−solid chemical reactions are removed via formation of product gases such as CO, CO_2, CH_4, C_2H_6, and so on, leaving no free carbon as volatile matter in the charred materials. Figure 3 presents the noncondensable gas yields for the broiler litter and cake samples as a function of pyrolysis temperature. Char and noncondensable gases yields were directly measured. All other gases, including the condensable gases such as reaction water and pyrolytic oil vapors, plus the noncondensable gases that were not calibrated, were considered as "condensable gas." These included tar and hydrocarbon gases greater than C_4H_{10} that were not quantified. The condensable gas yield that constitutes potential bio-oil or pyrolysis liquid was calculated as the difference between the biomass pyrolyzed and the sum of the measured gases and the residual char. Noncondensable gas yield increased for both samples with pyrolysis temperature and the increase was more significant for broiler litter than for broiler cake samples. Biogas yield was lower for broiler litter samples pyrolyzed at 700 °C, but at 900 °C noncondensable gas yield for broiler litter surpassed that of the broiler cake. Larger amounts of wood present in the broiler litter than broiler cake will decompose more completely at higher pyrolysis temperatures. Char yield was also a function of pyrolysis temperature. Char yield decreased with pyrolysis temperature with a much stronger decline observed for broiler cake char than broiler litter char. When comparing the char yields from the slow pyrolysis (Table 1) with those from the fast pyrolysis (Figure 3), it can be seen that there was a significant discrepancy. It is known that pyrolysis is a thermal process evolving in the absence of air which produces syn-gas, char, and tar in fractions that depend upon operating temperature, heating rate, and residence time. For high tar yields, a high heating rate and short residence time are requested (fast pyrolysis), whereas to maximize char and syngas yields, a low heating rate and a long residence time should be applied (slow pyrolysis).[20] Pyrolysis temperature also affected the amount of tar (condensable gases) produced (Figure 3). For broiler cake samples, significantly more bio-oil was produced as the temperature increased from 700 to 900 °C, whereas for broiler litter, there was only a slight increase (Figure 3). The mass balance on the broiler cake pyrolysis-products reveals that an increase in pyrolysis temperature translated predominantly into a mass conversion into condensable gases.

4. Gas Composition. Composition of the syn-gas will depend on the characteristics of the starting material. Syn-gas can be used as primary fuel for direct combustion. The main combustibles found in noncondensable gas are carbon dioxide, carbon monoxide, hydrogen, and low molecular weight hydrocarbons (HC). Compositional analysis of the noncondensable gas was important to determine the quality of the gas. Figure 4 presents the major components of the noncondensable gas produced by pyrolysis at three different temperatures, 700, 800, and 900 °C. These included CO, CO_2, and the low molecular weights hydrocarbon gases CH_4, C_2H_6, C_3H_8, and C_4H_{10} as well as hydrogen. The largest fraction of gas was carbon dioxide followed by carbon monoxide and then hydrocarbons, with hydrogen yields being the lowest for both samples. As Figure 4 shows, the CO_2 component of the noncondensable gas was lowest at the lowest temperature (700 °C) for both samples and increased with increasing pyrolysis temperature. The sharpest increase in carbon dioxide (approximately 50%) was observed for broiler litter samples from 800 to 900 °C. All the hydrocarbons increased with pyrolysis temperature as well, so did hydrogen. Even though it was represented in the lowest amounts measured, the percentage of hydrogen tripled from 700 to 900 °C with both samples. The increase of hydrocarbon yield with pyrolysis temperature is consistent with the depolymerization of larger molecular weight hydrocarbons (i.e., tars greater than C4) which would otherwise condense to form part of the bio-oil constituent.[13] The only measured gas that did not increase with pyrolysis temperature was carbon monoxide, where a slight (not significant) decrease was observed. The composition of the hydrocarbons consisted mainly of CH_4 with gradually smaller amounts of hydrocarbons of increasing number of carbon. Unless it can be converted to combustible gas products, CO_2 decreases the quality of syn-gas. For this reason, pyrolysis conditions that reduce the amount of CO_2 produced are favorable. Even though the amount of the primary combustible components of syn-gas (the lower molecular weight hydrocarbons, hydrogen, and carbon monoxide) increased in broiler litter and cake samples with increased temperature of pyrolysis, the same was not true in percentage terms. For broiler litter samples, the percentage of these components in the overall composition of the syn-gas, decreased from 37% to 34% for broiler cake and from 40% to 31% for broiler litter, when pyrolysis temperature increased from 700 to 900 °C. It is apparent that a higher quality syn-gas is produced for lower pyrolysis temperature.

Conclusions

In the present study, broiler manure is pyrolyzed to produce chars that possess enhanced adsorption ability for metal ions. These chars, without being subjected to subsequent activation, retained adsorption properties typically only associated with activated carbons. Their metal ion sequestering ability greatly exceeds that of chars made from traditional feedstocks such as coal, wood, and coconut shells, with Cu^{2+} adsorption between 0.33 and 0.91 mmol/g char. In contrast, chars produced from coal, coconut, or wood exhibited no detectable adsorption of Cu^{2+}. Slow pyrolysis of broiler manure entraps pre-existing phosphorus, primarily in the form of phosphate ions within the carbon matrix. It is postulated that the strategic exposure of chemical surface groups, such as phosphate, contributes significantly to the adsorption phenomena between charged species.

A mass balance on the char, syn-gas, and tar produced during pyrolysis revealed that yield for both condensable and noncondensable gases increased with pyrolysis temperature to the expense of a decrease in char yield. The change was much more significant for broiler cake than broiler litter. Pyrolysis temperature affected both char and syn-gas properties, with improved metal ion uptake contrasting with decreased syn-gas quality as pyrolysis temperature increased. Slow pyrolysis of broiler manure could possibly provide a char with enhanced ability to adsorb metal ions in addition to a syn-gas that can be used as a fuel.

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